

3548.04

MAR 2 8 2002

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TRANSMITTAL LETTER TO THE UNITED STATES/ELECTED OFFICE DO/EO/US

Applicants for DO/EO/US )  
 Mathias Pauls and Rene Schumacher ) Group Art Unit:  
 U.S. Serial No.: 08/\_\_\_\_\_ ) Examiner:  
 Filed: August 9, 1995 ) already  
 International Application No.: PCT/EP94/00385 ) entered.  
 International Filing Date: 10 February 1994 ) RJ  
 Priority Date Claimed: 10 February 1993 ) 4/23/02  
 For: PREPOLYMER COMPOSITION FOR )  
 INSULATING FOAMS )  
 \_\_\_\_\_

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DECLARATION THAT SUBSTITUTE SPECIFICATION  
CONTAINS NO NEW MATTER (37 CFR 1.125)

1. Identification of person making this declaration.

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The person making this declaration is the attorney in this application, registration number 29, 202.

## 2. Declaration

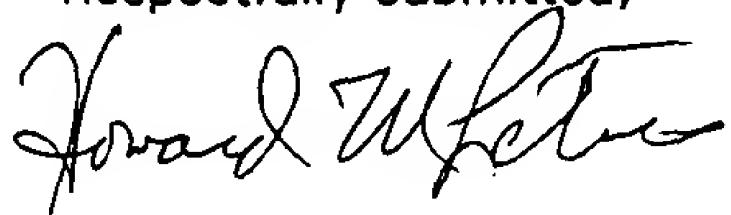
I hereby declare that the accompanying substitute specification contains no new matter over that contained in the above-identified PCT application originally filed in German and as translated into English.

[ ] I further state that the changes made are the same as indicated in the hand written interlined original specification also accompanying this declaration.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Futher, Declarant says not.

Respectfully submitted,



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HMP/eb.ref.1  
Enclosure: Substitute appl.

1

Description

2        This invention relates to a prepolymer composition for producing  
3        polyurethane insulating foams with fire-retardant properties from pressure  
4        tanks which consists of a prepolymer component with at least one PU  
5        prepolymer with a content of NCO groups of 4 to 20 wt% and usual additives  
6        as well as a propellant component. The invention furthermore relates to the  
7        use of softening phosphates and phosphonates as a fireretardant additive to  
8        prepolymer compositions for producing pressure-can polyurethane insulating  
9        foams, as well as to pressure cans with such a prepolymer composition for  
10      producing polyurethane insulating foams.

11       The inventive prepolymer composition is used for producing  
12      polyurethane insulating foams which are used particularly for insulating  
13      purposes by foaming in cavities. The main areas of application are the  
14      construction industry, but also technical products in which cavities must be  
15      filled to avoid condensation nests. When one-component polyurethane  
16      foams are spoken of, these are applied by discharging the prepolymer  
17      composition from pressure tanks, for example aerosol cans, on the spot with  
18      the help of propellants with a bulk density of 10 to 50 g/l, and processed. 1C  
19      foams are moisture-hardening, i.e. they can be cured solely with the help of  
20      the moisture contained in the air.

21       Two-component polyurethane foams require a second hydroxy  
22      component for curing the prepolymer composition, generally a polyol which  
23      must be added directly before foam formation. Curing can be accelerated by

1       catalysts. Bulk densities in 2C foams are characteristically 10 to 100 g/l.

2           Transitional forms between 1C and 2C foams are possible. In this  
3       case a quantity of a hydroxyl component insufficient for reacting the  
4       isocyanate groups is added to the prepolymer before discharge. Such "1.5C  
5       foams" are also covered by the invention.

6           Conventional prepolymer compositions for 1C and 2C  
7       polyurethane insulating foams contain a prepolymer component having a  
8       minimum content of reactive NCO groups. The prepolymer itself is a  
9       polymer of suitable viscosity with terminal NCO groups. Suitable isocyanates  
10      are for example isophorone diisocyanate, referred to as IPDI, tolylene  
11      diisocyanate, also referred to as TDI, diisocyanatotoluene, 1,5-diisocya-  
12      natonaphthalene, referred to as NDI, triisocyanatotrimethylmethane, 1,6-  
13      diisocyanatohexane, referred to as HDI, or 4,4diisocyanatodiphenylmethane  
14      in a raw and pure form or as a mixture. An especially common one is 4,4-  
15      diisocyanatodiphenylmethane, also referred to as MDI, which is used both in  
16      a raw form (raw MDI) and in the form of pure 2,4- and 4,4-isomers or  
17      mixtures thereof. One can likewise use the two common TDI isomers alone  
18      or in a mixture. For producing the prepolymer component one reacts such  
19      isocyanates with hydroxy polyethers, polyesters or polyvalent alcohols,  
20      making sure the prepolymer acquires a viscosity suitable for the composition.

21           Insulating foams to be used in the construction industry, so-called B2  
22       foams, must be set to be fire-retardant according to the national  
23       specifications. This is usually done by adding fire-retardant substances to the  
24       foaming materials, in particular chlorine- and bromine-containing organic  
25       compounds. Particularly well-known ones are chlorine and bromine  
26       derivatives from diphenyl ether and biphenyl, for example  
27       pentabromobiphenyl ether and polychlorinated biphenyls. Despite their

1 excellent fire-retardant properties these substances have fallen into dispute  
2 for toxicological reasons. If their approval has not yet lapsed, there are  
3 phasing-out deadlines. In addition, packings containing foamer residues  
4 polluted with such fire-retardant substances are subject to cost-intensive  
5 restrictions on disposal. The same applies to the finished foams when they  
6 are no longer needed and must be removed.

7 The problem of the invention is therefore to provide a PU prepolymer  
8 which can be set to be fire-retardant without using conventional chlorine-  
9 and bromine-containing organic materials and is thus halogen-free in the  
10 prepolymer component.

11 This goal is achieved with a prepolymer composition of the  
12 abovementioned type wherein the prepolymer component is substantially  
13 halogen-free and has a content of 5 to 40 wt%, based on the prepolymer  
14 component, of softening phosphates and/or phosphonates.

15 The inventively applied phosphates and phosphonates have the  
16 general formulae  $O=P(OR)_3$ , and  $O=P(OR)_2R$ , wherein R can have  
17 different meanings in one and the same molecule and means alkyl, aryl, alkyl  
18 aryl or aralkyl with up to 10 C atoms.

19 The inventive prepolymer compositions generally contain a PU  
20 prepolymer based on known aliphatic and aromatic polyisocyanates and  
21 polyester polyols. It has turned out that particularly polyester polyols make a  
22 considerable contribution to the fire-retardant standardization of the  
23 inventive prepolymer compositions.

24 For producing the inventively applied prepolymer composition one  
25 uses conventional aliphatic and aromatic polyisocyanates. In particular one  
26 uses polyfunctional isocyanates with a mean of 2 to 4 isocyanate groups, both  
27 in monomeric and in oligomeric form. As stated at the outset, these pre-

1 polymer compositions are themselves reaction products from monomers or  
2 oligomers containing isocyanate groups, and components reactive therewith,  
3 in particular hydroxyfunctional compounds. Suitable initial polyisocyanates  
4 are the ones mentioned at the outset and those stated for example in DE-A-  
5 42 15 647.

6 Especially suitable isocyanate prepolymers for these prepolymer  
7 compositions are ones based on HDI, MDI, TDI, NDI, 4,4'-  
8 dicyclohexylmethanediisocyanate and IPDI. The isocyanate prepolymers can  
9 be set to be low-monomer or substantially monomer-free. The NCO content  
10 in the applied prepolymer component is between 4 and 20 wt%, preferably  
11 between 6 and 18 wt% and in particular between 7 and 13 wt%.

12 When producing the isocyanate prepolymers one uses usual hydroxy  
13 components, for example polyether, polyester or modified vegetable oils with  
14 a sufficient hydroxyl number, approximately in the range of 100 to 300.  
15 Castor oil with a hydroxyl number of about 160 is suitable, as are usual  
16 glycols, in particular polyethylene glycols.

17 It is particularly suitable for inventive purposes to use polyesterols  
18 and native polyhydroxy compounds, which develop a synergistic effect with  
19 the inventively added softening phosphates and phosphonates. Polyester  
20 polyols that can be used are ones based on ethylene glycol or glycerine and  
21 aromatic or aliphatic, preferably native, polycarboxylic acids. These  
22 polyester polyols can be wholly or partly phosphorus-modified. Suitable  
23 polyester polyols have proved to be ones based on phthalic acid, isophthalic  
24 acid, terephthalic acid and adipic acid with molecular weights of 1000 to  
25 2000, the polyol component being generally provided by glycols, glycerine  
26 and butanediols in a monomeric or oligomeric form. It is also suitable to use  
27 polyhydroxy compounds based on aliphatic fatty acids and suitable

1 triglyceride derivatives, as are commercially available. The polyhydroxy  
2 compound applied in forming the prepolymer should have a hydroxy  
3 functionality in the range of 2 to 4.

4 The addition of a low quantity of polybutadiene makes it possible to  
5 improve the serviceability of the produced foams and obtain a fully  
6 foamable, dimensionally stable insulating material. Polybutadiene can be  
7 used in combination with PU prepolymers from all usual isocyanates, but is  
8 especially advantageous in combination with PU prepolymers based on HDI  
9 and MDI.

10 Suitable polybutadienes to be used are particularly liquid products as  
11 are offered by Hülls AG with a viscosity of at least 500 mPa.s at 20 °C.  
12 Viscosity is preferably at least 2000 mPa.s at 20 °C and in particular about  
13 3000 mPa.s at 20 °C. An especially suitable liquid polybutadiene is sold un-  
14 der the designation Polyol 130 with about 75% 1,4-cis double bonds, about  
15 24% 1,4-trans double bonds and about 1% vinyl double bonds and a  
16 molecular weight (vapor-pressure osmotic) of about 3000. The content of  
17 liquid polybutadiene according to the invention is 0.01 to 2 wt% and  
18 preferably 0.05 to 1 wt%, based on the prepolymer component to which it is  
19 added.

20 Suitable polybutadienes are furthermore those products of higher  
21 molecular weight which can be added to the prepolymer composition in a  
22 dissolved form or be dissolved therein. Also one

23 can use higher-molecular polymeric hydrocarbons containing double bonds.

24 The molecular weight of suitable stabilizing additives is expediently  
25 1000 to 9000, in particular up to 5000.

26 Along with pure (liquid) polybutadiene one can also use copolymers of

1       1,3-butadiene with other 1,3-dienes, for example isoprene, 2,3-  
2       dimethylbutadiene and piperylene, and with vinylaromatic compounds such as  
3       styrene, ( $\alpha$ -methylstyrene, vinyl toluene and divinylbenzene. The content of  
4       comonomers in the copolymers should not exceed 50 mol%. Such copolymers  
5       are regarded as falling within the designation "(liquid) polybutadiene" if they are  
6       liquid or soluble.

7           It is assumed that the dimensionally stabilizing effect of polybutadiene  
8       is based on its ability to crosslink in the presence of oxygen.

9           If a monomer-reduced prepolymer is used it is obtainable for example  
10      by removing the monomer in a thin-layer evaporator. Alternatively or  
11      additionally one can react (residual) isocyanate monomer with a hydroxy  
12      polyether and/or polyester and/or modified vegetable oil. Suitable  
13      vegetable oils are ones with a hydroxyl number of 100 to 300, for example  
14      castor oil with a hydroxyl number of about 160. According to the invention it  
15      is readily possible to obtain stable foams with such monomer-reduced  
16      prepolymer components, provided the polybutadiene is added. A  
17      prepolymer composition is termed low-monomer if it has less than 10%  
18      monomer, in particular less than 5% monomer; and substantially monomer-  
19      free if it has less than 2, preferably less than 1 and in particular less than 0.5  
20      wt% monomer, always based on the prepolymer component, i.e. the reactive  
21      isocyanate-containing component present in the composition.

22           The prepolymer can contain usual additives, for example  
23      polysiloxanes for cell regulation, further usual flameproofing agents,  
24      softeners, catalysts, viscosity regulators, dyes, rheology-controlling additives  
25      and the like. The prepolymer composition, i.e. the PU prepolymer including  
26      all additives without propellants, expediently has an initial service viscosity at  
27      20°C of 5000 to 20000 mPa.s and preferably of 8000 to 15000 mPa.s.

1 According to the invention the content of NCO groups in the PU prepolymer  
2 is 4 to 20 wt%, preferably 6 to 18 wt% and in particular 7 to 13 wt%, based  
3 on the prepolymer component.

4 To increase the fire-retardant effect of the insulating foams produced  
5 with the inventive prepolymer composition it may be expedient to add  
6 further flame-retardant additives which should also be free from chlorine and  
7 bromine in this case. It has proved particularly suitable to use melamine and  
8 melamine derivatives, for example melamine phosphate, dimelamine  
9 phosphate and melamine cyanurate, as well as cyanodiamide,  
10 dicyanodiamide, aluminum trihydrate, ammonium polyphosphate, in  
11 particular in a finely encapsulated form, and also red phosphorus. These  
12 agents are added in a finely divided form or as an emulsion. A wetting agent  
13 is generally likewise necessary for stabilizing the prepolymer composition.  
14 Conventional wetting agents can be used.

15 The inventive prepolymer composition contains in particular propane,  
16 butane and/or dimethylether as a propellant component. Further  
17 propellants that can be used in the component are fluorocarbons which are  
18 liquefiable under the pressure conditions prevailing in a pressure tank, for  
19 example R 125, R 134a, R 143 and R 152a. To minimize the content of  
20 combustible and halogen-containing propellants one can add further gases  
21 which are not condensable under the pressure conditions prevailing in the  
22 pressure can, for example CO<sub>2</sub>, N<sub>2</sub>O or N<sub>2</sub>-CO<sub>2</sub>, is particularly preferred since it  
23 can partly dissolve in the prepolymer component and thereby contribute to  
24 foam formation, while also acting as a good propellant. If fluorine-  
25 containing propellants are dispensed with, the entire prepolymer composition  
26 can be set to be halogen-free.

27 The propellant component of the prepolymer composition expediently

constitutes 5 to 40 wt%. The CO<sub>2</sub> content in the propellant can be for example about 5 wt%, based on the total propellant component. The content of gases not condensable under the prevailing pressure conditions should be such that the volume based on the empty space in the pressure tank yields a pressure of about 8 to 10 bars, depending on the relevant national specification for pressure tanks (aerosol cans). The empty space in the pressure tank is the space assumed by the uncondensed components of the prepolymer composition.

The liquid butadiene is optionally added to the prepolymer composition in solution along with an emulsifier - for example in a weight ratio of 80/20 -, preferably in solution with a hydroxy vegetable oil suitable for controlling the isocyanate content of the PU prepolymer. It has proven especially suitable to use castor oil with a hydroxyl number of 160, but any other hydroxy vegetable oils and hydroxy polyethers and polyesters can also be used. These are hydroxy components as are conventionally used for modifying viscosity in the formulation of prepolymer compositions.

The inventive prepolymer compositions can be used as 1C, 1.5C and 2C polyurethane foams. With 2C foams the polyol component required for curing the foam, and optionally a further component, are kept separate from the prepolymer composition in known fashion and added only directly before or during discharge. The corresponding methods are widely described and known to the expert, as are suitable two-component pressure cans with a separate tank for the second component.

The second component can be in particular usual polyols, in particular glycol, glycerine and butanediol. To accelerate the curing reaction it may be expedient to add to this second component a usual catalyst, for example tin dioctoate, cobalt naphthenate and octoate, dibutyl tin dilaurate, metallic, in

1 particular ferrous, acetonylacetate, DABCO crystalline and N-methyl-2-  
2 azanorbornane. Further catalysts are triethylenediamine, trimethylamino ethyl-  
3 piperazine, pentamethyldiethylenetri amine, tetramethyliminobis-propylamine,  
4 bis(dimethylaminopropyl)-N-isopropanolamine. It is also suitable to use het-  
5 eroaromatic amines, as stated for example in DE-A-42 15 647.

6 The invention relates finally to the use of softening phosphates and  
7 phosphonates, as defined above, for setting polyurethane insulating foams to  
8 be fire-retardant. The invention also relates to pressure cans for discharging  
9 polyurethane insulating foams which are filled with a prepolymer  
10 composition and optionally a separate polyol component, as described above.

11 The inventive prepolymer compositions have the advantage that they  
12 can be produced substantially free from chlorine and bromine and can still  
13 be set to be fire-retardant without a need to add the usual halogen-  
14 containing flameproofing agents. This means that the addition of  
15 flameproofing agents for B2 foams according to DIN 4102 can be largely or  
16 fully dispensed with. If necessary, the prepolymer compositions can also be  
17 set to be substantially halogen-free, i.e. one can dispense not only with  
18 halogen-containing flameproofing agents but also with fluorocarbons as  
19 propellants. In this case it is sufficient for the propellant component to  
20 contain propane, butane, dimethylether and/or CO<sub>2</sub>.

21 It has turned out that these flame-retardant properties are due in  
22 particular to the trialkyl and triaryl phosphates and phosphonates. One can  
23 mention diphenylcresyl phosphate, triphenyl phosphate, tricresyl phosphate,  
24 triethyl phosphate, dimethylmethane phosphonate, diethylethane  
25 phosphonate and the like. One can further mention 2-  
26 ethylhexyldiphenylphosphate and phosphoric acid-1,3-  
27 phenylenetetraphenylester, which are commercially available under the

1 designations Posflex 362 and Fyroflex RDP. Such phosphates and  
2 phosphonates are present in the prepolymer composition in a quantity of 5 to  
3 40 wt%, based on the prepolymer. They have the advantage that they do not  
4 disturb the balance of prepolymer, propellant and thinners in the prepolymer  
5 composition but rather stabilize it, while conventional halogen-containing  
6 flameproofing agents interfere with this balance and can only be present with  
7 about 12 to 14 wt%. At the same time they have a softening function.

8 The inventive prepolymer composition is produced in the fashion  
9 known in the art, whereby if low-monomer prepolymer is used it is put in the  
10 pressure tank as such or arises therein. One then optionally adds to the  
11 prepolymer the liquid polybutadiene, e.g. mixed with a surface-active agent  
12 and emulsified in a hydroxy oil, for example castor oil. The hydroxy oil or  
13 castor oil simultaneously serves to finely adjust the NCO content of the  
14 prepolymer and lower the monomer content. Then the additives, such as  
15 flameproofing agents, stabilizers, softeners, catalysts, etc., are added,  
16 whereupon the pressure tank (aerosol can) is sealed and the propellant  
17 impressed.

18 The invention will be explained by the following compositions.

19 Examples 1 and 2

20 Desmodur 44 V 20 L, a polyisocyanate with 31.6 wt% NCO groups  
21 from Bayer, is mixed in a protective atmosphere with the polyol component.  
22 The latter consists of Desmophen PU 578, a polyol with the hydroxyl number  
23 213, castor oil with a hydroxyl number of 155, diphenylcresyl phosphate as a  
24 softener and flame-retardant (Disflamoll DPK), a usual polysiloxane for  
25 stabilization (Tegostab BF 2270, hydroxyl number 40) and a 10% emulsion of

1 a liquid polybutadiene with a molecular weight of about 3000 and a viscosity  
 2 at 20 °C of 3000 mPa.s in castor oil (Tego IMR 830 from Goldschmidt;  
 3 weight ratio polybutadiene/emulsifier 80/20). As a catalyst Texacat  
 4 DMDEE (2,2-dimorpholinodiethylether) is added.

5	Component	Example 1	Example 2
6			
7	Desmophen PU 1578	380	380
8	Disflamoll DPK	543	273
9	Fyroflex RDP	-	270
10	Tegostab BF 2270	20	20
11	Tego IMR 830 (10%)*	50	50
12	Texacat DMDEE	7	7
13			
14	Polyol mixture (parts by weight)	1000	1000
15			
16	Polyol mixture	275 g	275 g
17	Desmodur 44 V 20 L	385 g	385 g
18	R 134a	75g	75 g
19	i-butane	30g	30 g
20	Dimethylether	35g	35 g
21			
22	Total	800 g	800 g
23			
24	<u>Example 3 to 7</u>		
25	Inventive prepolymer compositions were produced by the following		
26	recipes analogously to Examples 1 and 2. The compositions yield a fire-		
27	retardant insulating foam with good insulating properties.		
28	Desmophen PU 1578 designates a polyester polyol based on phthalic		
29	acid/adipic acid with the hydroxyl number 213, Amgard V 82 a phosphorus-		
30	modified polyol with the hydroxyl number 110, Unichema VCN 90.243 a		
31	hydroxy component with the hydroxyl number 107 based on ethylene glycol		

24 Example 3 to 7

25 Inventive prepolymer compositions were produced by the following  
 26 recipes analogously to Examples 1 and 2. The compositions yield a fire-  
 27 retardant insulating foam with good insulating properties.

28 Desmophen PU 1578 designates a polyester polyol based on phthalic  
 29 acid/adipic acid with the hydroxyl number 213, Amgard V 82 a phosphorus-  
 30 modified polyol with the hydroxyl number 110, Unichema VCN 90.243 a  
 31 hydroxy component with the hydroxyl number 107 based on ethylene glycol

1        adipates and native fatty acids, Sovermol 1068 an aliphatic triglyceride based  
 2        on soy oil with the hydroxyl number 190, Sovermol 1072 N an aliphatic fat-  
 3        chemical polyester triol with the hydroxyl number 100, and castor oil one  
 4        with the hydroxyl number 155. The propellant is the mixture of Examples 1  
 5        and 2.

6	Components	Parts by weight				
7		3	4	5	6	7
9	Desmophen PU	280		200	300	223
10	Amgard V 82	100				
11	Desmophen VPPU		550		223	
12	Unichema VCN			200		
13	Sovermol 1068					100
14	Sovermol 1072/V					150
15	Castor oil			200		
16	Disflamoll	543	373	323	400	450
17	Tegostab BF 2270	20	20	20	20	20
18	Tego IMR 830 (10%)	50	50	50	50	50
19	Texacat	7	7	7	7	7
20						
21	Polyol component 3/17	1000	1000	1000	1000	1000
22	Polyol component 3/17	275 g	280 g	280 g	280 g	280 g
23	Desmodur 44 V 20 L	385 g	380 g	380 g	380 g	380 g
24	Propellant	140 g	140 g	140 g	140 g	140 g
25						
26	Total	800 g	800 g	800 g	800 g	800 g
27	NCO (wt%)	15.7	16.0	14.9	15.1	15.3

1	2	3	Parts by weight				
			8	9	10	11	12
4	Component						
5	Desmophen PU	300	223	223	300	300	
6	Amgard C 82					100	
7	Desmophen VPPU		200	200			
8	APP 200 B	200					100
9	Prilast 3185						
10	Sovermol 1068			100			
11	Castor oil		100			200	
12	Disflamol DPK	423		250			
13	TKP	300				423	
14	TPP			423			
15	Fyroflex RDP		100				
16	Phosflex 362			150			
17	Tegostab BF 2270	20	20	20	20	20	
18	Tego IMR 830 (10%)	50	50	50	50	50	
19	Texacat DMDEE	7	7	7	7	7	
20	Polyol component 8/12	1000	1000	1000	1000	1000	
21	Polyol component 8/12	275 g	300 g	280 g	280 g	270 g	
22	Desmodur						
23	44 V 20 L	385 g	370 g	380 g	380 g	380 g	
24	Propellant	140 g	140 g	140 g	140 g	140 g	
25	Total	800 g	810 g	800 g	800 g	790 g	
26	NCO (wt%)	14.9	14.3	15.1	14.9	14.5	

28           Inventive prepolymer composition were produced by the following  
 29           recipes analogously to Examples 1 and 2. The Compositions yield a fire-  
 30           retardant insulating foam with good insulating properties.

31           The softeners used are diphenylcresyl phosphate (Disflamol DPK),  
 32           tricresyl phosphate (Disflamol DPK), triphenyl phosphate (20% in DPK,

1 Disflammol TPP), dimethylmethane phosphonate (Amgard DMMP),  
 2 phosphoric acid-1,3-phenylenetetraphenylester (Fyroflex RDP) and 2-  
 3 ethylhexyldiphenylphosphate (Phosflex 362). APP 200 B designates an  
 4 aromatic polyester polyol from Union Carbide, Priplast 3185 a polyhydroxy  
 5 compound based on ethylene glycol adipate and dimeric fatty acids from  
 6 Unichema.

8	Component	Parts by weight				
		13	14	15	16	17
10	Desmophen PU	300	300	300	300	300
11	Disflammol DPK	468	468	468	468	468
12	Melamine cyanurate	150				75
13	Securoc A 5 F		150			75
14	Cyanodiamide			150	150	
15	Hostaflamm					
16	Tegostab BF 2270	20	20	20	20	20
17	Wetting agent	5	5	5	5	5
18	(BYK 160)	50	50	50	50	50
19	Tego IMR 830(10%)		7	7	7	7
20	Texacat DMDEE					
21						
22	Polyol component 13/17	1000	1000	1000	1000	1000
23	Polyol component 13/17	310 g	310 g	310 g	310 g	310 g
24	Desmodur					
25	44 V 20 L	360 g	360 g	360 g	360 g	360 g
26	Propellant	140 g	140 g	140 g	140 g	140 g
27						
28	Total	810 g	810 g	810 g	810 g	810 g
29	NCO (wt%)	14.5	14.5	14.5	14.5	14.5

30 Inventive prepolymer compositions were produced by the following recipes  
 31 analogously to Examples 1 and 2. The compositions yield a fire-retardant  
 32 insulating foam with good insulating properties.

1 Securoc A 5 F designates an aluminum trihydrate and Hostaflamm AP 462 an  
2 ammonium polyphosphate in an encapsulated form or functionally modified on  
3 the surface. The propellant mixture is the same as in Examples 1 and 2.

4 With constant stirring the desired quantity of the above-described  
5 mixture is put in a moisture-free pressure tank which is sealed with a dome  
6 provided with a valve, optionally with introduction of a cartridge having the  
7 second component. After sealing, a corresponding quantity of propellant is  
8 impressed. The individual components of the propellant mixture are  
9 expediently impressed successively and optionally filled up again in a second  
10 pass. An especially suitable mixture is of 21.5% i-butane and 28.5%  
11 dimethylether and 50% fluorocarbon.

12 In the following monomer-reduced prepolymer compositions and filling  
13 proportions for a pressure tank with a filling ratio of 75% are stated. Both  
14 compositions yield an insulating foam with good service properties.

15

Claims

1. A prepolymer composition for producing polyurethane insulating foams with fire-retardant properties from pressure tanks which consists of a prepolymer component with at least one PU prepolymer with a content of NCO groups of 4 to 20 wt% and usual additives, as well as a 5 propellant component, characterized in that the prepolymer component is substantially halogen-free and has a content of 5 to 40 wt%, based on the prepolymer component, of softening phosphates and/or phosphonates with the formulae  $O=P(OR)_2$ , and  $O=P(OR)_2R$ , wherein R, identically or differently, means alkyl, aryl, alkyl aryl or aralkyl with up to 10 C atoms.

2. The prepolymer composition of claim 1, characterized by a PU prepolymer based on aliphatic and aromatic polyisocyanates polyester polyols.

3. The prepolymer composition of claim 2, characterized in that the polyisocyanate is one based on hexamethylene-1,6diisocyanate, naphthalene-1,5-diisocyanate, tolylene diisocyanate, isophorone diisocyanate, diphenylmethane diisocyanate or dicyclohexylmethane diisocyanate.

4. The prepolymer composition of claim 2 or 3, characterized in that the polyester polyols have a molecular weight of 1000 to 2000.

5. The prepolymer composition of any of claims 2 to 4, characterized in that the polyester polyols are ones based on ethylene glycol or glycerine and aromatic or aliphatic, preferably native, polycarboxylic acids.

6. The prepolymer composition of any of claims 2 to 5, characterized in that the polyester polyols are at least partly phosphorus-modified.

7. The prepolymer composition of any of the above claims, characterized by a content of liquid polybutadiene of 0.01 to 2 wt%.

8. The prepolymer composition of claim 7, characterized in that the liquid polybutadiene contains about 75% 1,4-cis

double bonds, about 24% 1,4-trans double bonds and about 1% vinyl double bonds, has a molecular weight, determined by vapor-pressure osmosis, of about 5 3000 and a viscosity at 20°C of about 3000 mPa.s.

9. The prepolymer composition of any of the above claims, characterized by a propellant content of 5 to 40 wt%.

10. The prepolymer composition of any of the above claims, characterized in that the propellant component contains propane, butane and/or dimethylether.

11. The prepolymer composition of any of the above claims, characterized in that the propellant component contains fluorocarbon, in particular R 125, R 134a, R 143 and/or R 152a.

12. The prepolymer composition of any of the above claims, characterized in that it additionally contains a flame-retardant additive which is free from chlorine and bromine.

13. The prepolymer composition of claim 12, characterized in that the flame-retardant additive is melamine, melamine cyanurate, dimelamine phosphate, melamine phosphate, cyanodiamide, dicyanodiamide, aluminum trihydrate, ammonium polyphosphate or a mixture thereof.

14. The prepolymer composition of any of the above claims, characterized by an initial service viscosity of the PU prepolymer at 20°C of 5000 to 20000 mPa.s.

15. The prepolymer composition of claim 11, characterized by an initial service viscosity of the PU prepolymer of 8000 to 15000 mPa.s.

16. Use of softening phosphates and phosphonates as defined in claim 1 for setting polyurethane insulating forms to be flame-retardant.

17. A pressure can for discharging 1C polyurethane insulating foams, filled with the prepolymer composition of any of claims 1 to 15.

1      Abstract

2            A prepolymer composition for producing polyurethane insulating foams  
3        with fire-retardant properties from pressure tanks which consists of a prepolymer  
4        component with at least one PU prepolymer with a content of NCO groups of 4 to  
5        20 wt% and usual additives, as well as a propellant component, wherein the  
6        prepolymer component is substantially halogenfree and has 5 to 40 wt%, based on  
7        the prepolymer component, of softening phosphates and/or phosphonates with the  
8        formulae O=P (OR)<sub>3</sub> and O=P (OR)<sub>2</sub>R.

9        HMP/eb.1

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## DECLARATION

2 I, Dr. Monica Koch, of Alte Allee 47, 81245 Munich, Germany, do hereby declare that I  
3 am conversant with the English and German languages and that I am a competent translator  
4 thereof.

5 I verify that the attached English translation is a true and correct translation of the German  
6 patent application entitled "Prepolymerzusammensetzung für Dämmeschäume".

7

27 July 1995